Analytical Methods

Total Extractable Petroleum Hydrocarbons

NJ-TPH-QAM 025-10/91

New Jersey Department of Environmental Protection
Office of Quality Assurance
Analytical Method

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Title:
Quantitation of
Semi-Volatile
Petroleum Products in
Water, Soil, Sediment
and Sludge

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1.0 SCOPE OF APPLICATION

1.1 Scope

This method utilizes a gas chromatograph fitted with a flame ionization detector (FID). The following petroleum analyses are included in the method:

1.1.1 Quantitative analysis of environmental samples (water, soil, sediment, and sludge) for residues from commercial petroleum products such as crude oil, diesel fuel, waste oil, fuels oils Nos. 2-6, lubricating oil, processed oils and bunker fuel.

The method determines Total Semi-Volatile Petroleum Products (TPHC), also known as Total Petroleum Hydrocarbons. TPHC includes paraffinic, naphthenic, and polynuclear aromatic hydrocarbons (PAHs).

The method must not be used for gasoline contaminated sites.

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1.1.2 Fingerprint - Identification of unknown petroleum products by comparison of their chromatograms with chromatograms of known petroleum product profiles. Products that can be identified include diesel fuel, fuel oils Nos. 2-6, lubricating oils, bunker fuel and processed oils (2).

1.2 Applicable Program

Underground Storage Tanks (UST), New Jersey Spill Fund, Comprehensive Environmental Response Compensation and Liability Act (CERCLA), Industrial Site Recovery Act (ISRA), Sludge Residuals, and Resource Conservation and Recovery Act (RCRA).

1.3 Method Advantages

1.3.1 The method replaces the TPHC method based on Freon 113 extraction and analysis by infrared spectroscopy.

1.3.2 The FID response produces a TPHC chromatogram that can be used to identify the type of petroleum product present by matching the chromatogram of the unknown sample with the chromatograms of known petroleum products.

1.4 Method Limitations

1.4.1 Quantitative Studies

1.4.2.1 The TPHC is quantitatively restricted to the semi-volatile components since partial loss of volatiles (b.p. < 60°C) occurs during the extraction and/or concentration process.

1.4.2.2 The gas chromatographic conditions are not designed for compounds with carbon numbers greater than C40.

1.4.2.3 Benzene and hydrocarbons that elute from the column before heptane co-elute with the extraction solvent methylene chloride.

1.4.2 Identification Studies

1.4.1.1 The method is most successful with fresh spills of petroleum products. Weathering changes the chromatographic profile. Weathering can be simulated in the laboratory.

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1.4.1.2 Absorption, adsorption, biological reactions, and chemical reactions occur in soil, changing the chromatographic profile which reduces the ability to make positive identifications. Method OQA-QAM-018 can be used for more detailed product analysis.

1.5 · Matrix

1.5.1 Surface water, ground water, and wastewater.

1.5.2 Soil, sediments or high solids sludge (>50%).

2.0 SUMMARY OF METHOD

2.1 This quantitative TPHC method is adopted from the "Leaking Underground Fuel Tanks Field Manual" of the California State Water Resources Control Board (3). This method is also derived from "Test Methods for Evaluating Solid Waste" USEPA Method 8015B and the Florida Department of Environmental Protection, "Method for the Determination of Total Petroleum Range Organics"(4, 25).

2.2 This petroleum method is adapted with modifications from ASTM Method D3328-82, and the US Coast Guard Oil Spill Identification Procedure for Total Petroleum (1,2).

2.3 Petroleum residues are extracted from sample matrices with methylene chloride. Surrogate compounds are added to all samples before extraction. The methylene chloride extract is analyzed with a gas chromatograph fitted with a capillary column attached to a FID.

2.3.1 The TPHC is determined by integration of the FID chromatogram. Calibration of the gas chromatograph is done with a hydrocarbon standard C8-C40 or where justified and documented, based on historic site-specific data, a standard reference petroleum product.

2.3.2 Identification of unknown residues may be done by comparing their chromatograms with chromatograms of known petroleum products. Samples from old spills are compared to synthetically weathered samples if available. Identification is established when chromatograms match. Method QAM-018 must be used for detailed pattern recognition (6).

2.3.3 The sensitivity of the method is dependent on the level of interference rather than on instrumental limitations. The method detection limit (MDL) for TPHC in soil is approximately 10 ug/g and in water 30 ug/L. These MDLs can be achieved without concentrating the extract.

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2.3.4 Dynamic Range

2.3.4.1 TPHC

Soil   30-1000 ug/g
Aqueous 0.1-500 mg/L

2.3.4.2 Individual Compounds

Soil   1.0-500 ug/g
Aqueous 0.2-200 ug/L

3.0 INTERFERENCES

3.1 Method interferences are reduced by washing all glassware with hot soapy water and then rinsing with tap water, distilled water, methanol, and methylene chloride.

3.2 High purity reagents such as Burdick and Jackson GC2 methylene chloride, Baker capillary grade methylene chloride or equivalent must be used to minimize interference problems.

3.3 Before processing any sample, the analyst should demonstrate daily, through the analysis of a method blank, that the entire system is interference-free.

3.4 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interference will vary considerably from source to source (e.g. fatty acids, biogenic materials, oxidized biodegradation products), depending upon the nature and diversity of the site being sampled. The cleanup procedure, EPA Method 3630B can be use to overcome many of these interferences, but unique samples may require additional cleanup approaches to achieve the method detection limit (MDL) (4).

3.5 Naturally occurring alkanes may be detected by this method and may interfere with product identification. Naturally occuring plant waxes include odd carbon number alkanes from n-C_{25} through n-C_{35}, and exhbit a dominant odd/even chain length distribution. Leaf hydrocarbons also may be detected.

3.6 A vial septum should be penetrated and extracted with methylene chloride to evaluate the potential alkane distribution that could occur in re-analyzed extracts. Vial septums should be changed after each analysis.

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3.7 Particulates interfer with the determination of disolved petrolem products in ground water. Petroleum products adsorb on the surface of particulates. The groundwater samples should be filtered through glass fiber filters to determine dissolved TPH.

4.0 SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been defined precisely. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Additional reference to laboratory safety are available and have been identified for use by the analyst (8,9).

5.0 APPARATUS AND EQUIPMENT

5.1 Sampling Containers

5.1.1 Prior to use, wash bottles and cap liners with aqueous detergent solutions and rinse with tap water, distilled water, and methylene chloride. Allow the bottles and containers to air dry at room temperature, place in a 150°C oven for one hour, then remove and allow to cool in an area known to be free of organic analytes.

5.1.2 Screw cap bottle - 40 mL PTFE-faced silicone cap liners.

5.1.3 Narrow mouth bottles - 1 liter, amber, PTFE faced silicone cap liners.

5.1.4 Wide-mouth glass jar-four ounce, amber, PTFE faced silicone cap liners

5.2 Glassware

5.2.1 Serum bottles - 100 mL, 10 mL, 2 mL crimp-top, PTFE-faced silicone cap liners.

5.2.2 Pasteur pipets

5.2.3 Screw-cap Erlenmeyer flasks - 250 mL, with PTFE faced silicone cap liners.

5.2.4 Volumetric flasks - 10 mL, 25 mL, 100 mL

5.2.5 Kuderna-Danish apparatus (KD)

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5.2.6 Sepratory funnels - 2 L Pyrex, Teflon stopcoat

5.2.7 Soxhlet Extractor

5.3 Apparatus

5.3.1 Rotary shaker table, 350 rpm minimum

5.3.2 Analytical balance capable of accurately weighing 0.0001 g.

5.3.3 A gas chromatograph with split/splitless injector, equipped with a capillary column, capable of temperature programming.

5.3.3.1 Column-30m long x .53mm ID, .5um film thickness dimethyl polysiloxane coating (Restek, J&W Scientific or equivalent). This column will allow for the resolution of alkanes from nC8 to nC40, as well as the resolution of phytane/nC18 and pristane/nC17. This column will also allow for the resolution of the petroleum products listed in Section 1.1 (21). Low bleed columns must be used. Equivalent columns maybe used.

5.3.3.2 Column - 30m long x 0.32mm ID, 0.25um film thickness, 95% dimethyl-5% diphenyl polysilxane (J&W Scientific, Restek or equivalent). This column has simillar resolution to 5.3.3.1 but high bp compounds elute later. Equivalent columns maybe used.

5.3.3.2 Column - 100m long x .25mm ID., 0.5um film thickness, capillary, Protocol DH (Supelco or equivalent (22).

5.3.3.3 Detector - Flame Ionization Detector (TPHC only)

5.3.4 An autosampler is recommended.

5.3.5 Boiling chips - Solvent extracted approximately 10/40 mesh.

5.3.6 Water bath - Top, with concentric ring cover, capable of temperature control. The bath should be used in a hood.

5.3.7 Gas-tight syringe - One milliliter (mL) with chromatographic needles.

5.3.8 Microsyringes – 10uL, 100uL, 200uL

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5.3.9   Continuous liquid-liquid extraction apparatus.

5.3.10   Liquid chromatographic column - 400 x 20mm with course frit, teflon stopcock.

5.3.11   Magnetic stirrer and 2-inch Teflon coated stirring bars.

5.3.12   Nitrogen concentration system composed of a precleaned pasteur pipet, with a small plug of glass wool loaded at the tip end, and filled with approximately 1-2 cm of precleaned alumina. The top of the pipet is attached to a hydrocarbon free nitrogen gas source using precleaned Teflon tubing. This concentration step should be performed at room temperature or lower to retain light end compounds.

6.0   REAGENTS

6.1   Purity of Reagents - Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee and Analytical Reagents of the American Chemical Society.

6.2   Reagent water - Reagent water is defined as a water in which an interference is not observed at the MDL of each parameter of interest. (ASTM Specification D1193, Type ii).

6.3   Methylene chloride, methanol, carbon, disulfide and hexane - pesticide grade, Burdick and Jackson GC2, Baker Capillary Grade or equivalent.

6.4   Sodium sulfate - (ACS) granular, anhydrous. Purify by heating at 400°C for four hours in a shallow tray, cool in a desiccator and store in a sealed glass bottle.

6.5   Silica gel - Grade 923 (100/200) desiccant. Before use, activate for at least 16 hours at 130°C in a shallow glass tray that is loosely covered in foil. Cool and store as in Section 6.4.

6.6   Silica granular, fine (60-120 mesh) Fisher 5151-10. Purify by Soxhelt extraction with methylene chloride for four hours. Dry at 80°C. Store in glass bottle.

6.7   Hydrochloric acid, 1:1 - Mix equal volumes of (ACS) concentrated HCl and distilled water.

6.8   Stock Standards

6.8.1   Normal Paraffinic Hydrocarbons - Prepare a Methylene chloride solution containing a mixture of components ranging from octane to tetracontane

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(nC8-nC40), or selected individual normal paraffins (2 mg/ml ea). The standard must include a minimum of 12 compounds including C8, C18, C20, C32, and C40. For product identification purposes the mixture also may contain C17, pristane and phytane (2 mg/ml ea.). A separate pristane, phytane, C17, and C18 column resolution standard may be used. An appropriate dilution of the mixture is analyzed under normal analytical conditions to determine retention times and the Relative Response Factors for the Compounds. A 10% carbon disulfide/ 90% methlyene chloride solvent mixture may be used if standard do not remain in solution. (Mixtures are available from Supelco, Restek (31266), NSI Solutions and Ultrex).

6.8.2 Diesel and Fuel Oil Profile Standards - Where applicable prepare commercial diesel, waste motor oil and/or fuel standards in methylene chloride. Weigh 300mg oil to the nearest 0.1 mg, into a 10 mL volumetric flask. Dilute to volume with methylene chloride (30 mg/ml). Standards are available from Restek Inc., Bellefonte, PA.

6.8.3 Surrogates (SS) and Internal Standards (IS) - The surrogates (chlorobenzene, ortho-terphenyl [OTP] and tetracosane-d50), and internal standard (5-androstane) are prepared separately by carefully weighing 100 mg of each compound in a 100 mL volumetric flask. Dilute to volume with methylene chloride. The final concentration of each compound is one ug/uL. The laboratory is free to choose any two or more surrogates that cover the carbon range (C8 - C40). However chlorobenzene is required. Standards are available from Restek Inc.

6.8.4 Quality Control Check Standard (Blank Spike) - The QC check standard concentrate (30 mg/ml) of fuel oil #2 must be prepared by the laboratory using stock standards prepared independently from those used for calibration (Section 6.8.2). If the contamination at the site is known, other fuel standards can be used. Standards are available from Supelco, Restek or Ultrex.

6.8.5 Matrix spiking standard (MSS) - Prepare the MSS in methylene chloride from a Fuel oil #2 standard in Section 6.8.2 or another oil for site speific work. The laboratory may use the hydrocarbon calibration standard noted in section 6.8.1 as the MSS for unknown petroleum sources.

7.0 CALIBRATION

7.1 Initial Calibration

7.1.1 Rentention time windows

a.　Before establishing windows, make sure the GC system is within optimum operating conditions. Serial injections over less than a 72 hr period result in retention time windows that are too tight.

b.　Calculate the mean and the standard deviation of the three retention times (use any function of retention time; including absolute retention time, or relative retention time) for each surrogate.

c.   Plus or minus three times the standard deviation of the mean retention times for each surrogate will be used to define the retention time window; however, the experience of the analyst should weigh heavily in the interpretation of chromatograms. The default value for the retetion time shall be a minimum of +/- 0.05 minutes, if the standard deviation is zero.

d.   Establish the midpoint of the retention time window for each surrogate by using the absolute retention for each surrogate from the mid-concentration standard of the initial calibration. The absolute retention time window equals the midpoint $\pm$ 3 SD, where the standard deviation is determined as described in Section b.

e.   The laboratory must calculate retention time windows for each surrogate on each GC column and whenever a new GC column is installed. The data must be retained by the laboratory.

7.1.2   FID Internal Standard Calibration for Quantitation of TPHC - Calibrate the GC-FID with an initial fivepoint, (i.e., concentration of individual components 1 ng/uL, 5ng/uL, 10ng/ul, 20 ng/uL, 50ng/uL), Total Petroleum Hydrocarbons calibration curve (Section 6.8.1). The lowest concentration point in the calibration curve should be near the MDL. The highest concentration point should be twice the expected sample concentration and within the linear instrument range. To maintain the standards in solution, a 10% carbon disulfide/90% methylene chloride solvent may be required. Prepare the calibration standard to contain 5.0 ng/ul of surrogate and GC internal standard. The relative standard deviation (RSD) for the surrogates and each calibration compound's relative response factor (RRF) must be less than or equal to 20%. If not, the calibration curve must be used to determine concentration. A minimum correlation coeffient of 0.95 is required. Also calculate the response for total petroleum hydrocarbons (TPHC) which is the average of the RRFs for the nC8-nC40 compounds (Section 11.2.2). The RSD must be less than 20%. The chromatograms should be checked for mass discrimination (Section 7.3). Standards with concentrations greater than 20 mg/L may need to be equilibrated to room temperature prior to analysis.

7.1.3   TPHC External Standard Calibration - The laboratory has the option of using an external calibration procedure. Prepare the standards as directed in Section 7.1.2 omitting the internal standard. Calculate response factors (RF) instead of relative response factors for each compound and the surrogates. The relative standard deviation (RSD) of each calibration compound's response factor (RF) must be less than 20%. If not the calibration curve must be used to determine concentration. A minimum correlation coefficient of 0.95 is required. Also

calculate the response for total petroleum hydrocarbons (TPHC) which is the average of the RFs for the nC8-nC40 compounds (Section 11.3).

7.1.4 TPHC Petroleum Product Calibration - If the laboratory has a site specific project and the petroleum product contamnation is known the GC_FID maybe calibrated using a reference petroleum product (Section 6.8.2). Calibrate the GC-FID with an initial five point, (i.e. concentration total petroleum 0.1 mg/ml, 0.2mg/ml, 1.0mg/ml, 2.0mg/ml, 5.0mg/ml) calibration curve. Calculate the response factor (RF) for TPHC (Section 11.2). The RSD of the TPHC responce factor must be less than 20%. If not the calibration curve must be used to detirmine concentration. A minimum correlation coefficient of 0.95 is required.

7.1.5 Petroleum Profile Calibration - If the method is used only for qualitative petroleum product profiling, a single point GC-FID retention time calibration is required. Prepare a 2 mg/ml standard from the products in section 6.8.2 (23). Prepare a 20 ng/ul carbon number standard from section 7.12.

7.2 Daily Calibration

7.2.1 The resolution check is required for fingerprint determination. The resolution of the chromatographic column should be checked daily. Inject two uL of the calibration mixture (10 ng/ul) (section 7.1.2) into the chromatograph. Visually inspect the chromatograms for separation between phytane and nC18.

If a standard fuel oil #2 is used as the calibration mixture, the resolution of the chromatograph column can be monitored by visually checking the resolution of the pair, nC17-Pristane and nC18-phytane. These compounds occur in all fuel oil #2 products.

7.2.2 The working calibration curves or calibration factors for TPHC, must be verified on each working day and after every 12 hours by the measurement of one or more calibration standards, (10 ng/ul). Calculate the percent difference (D%) between the verified RF/RRF and the inital responses RF/RRF for TPHC and the surrogates. The %D must not exceed 20%. If the %D exceeds 20% the instrument must be recalibrated. Reanalysis of all samples analyzed after a non compliant standard is required.

7.2.3 The retention times of surrogates in the calibration verification standard analyzed at the beginning of the analytical shift must fall within the absolute retention time windows calculated in Sec. 7.1.1b. The purpose of this check is to ensure that retention times do not continually drift further from those used to established the widths of the retention time windows. If the retention time of any surrogate at the beginning of the analytical shift does not fall within the ± 3 SD

window (minimum +/- 0.05 min.), then a new initial calibration is necessary unless system maintenance (Sec. 7.11) corrects the problem.

In addition, the retention times of all surrogates in the subsequent calibration verification standards analyzed during the analytical shift must fall within the absolute retention time windows established in Sec. 7.1.1d.

7.2.4 Surrogate Standards (SS), GC Internal Standard (IS) - The SS and IS responses and retention times in the calibration check standard must be evaluated during or immediately after data acquisition. If the retention time(s) for the SS or IS is outside the determined RT window, the chromatographic system must be inspected for malfunctions and corrections must be made. If the area(s) for the SS or IS changes by +/- 50% from the last daily calibration standard check, the GC must be inspected for malfunctions and corrections must be made.

7.3 Mass Discrimination

7.3.1 Mass discrimination can take place in the injection port. The heavier molecules do not enter the column as a defined plug of vapor with the lighter molecules.

7.3.2 Mass discrimination is minimized by placing a small plug of silanized glass wool one centimeter from the base of the glass injection liner. The end of the capillary column is placed just below the glass wool.

7.3.4 The calibration chromatogram (Section 7.1.1) is inspected for mass discrimination. The response factor ratio C32/C20 should be greater than 0.8. If the ratio is less, reposition the column in the glass liner until mass discrimination is minimized.

8.0 QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality control program which conforms with New Jersey Regulation N.J.A.C. 7:18-4.7 (13). The minimum requirements of this program consist of an initial demonstration of laboratory capability and an ongoing analysis of QC samples to evaluate and document data quality. The laboratory must maintain records to document the quality of data that is generated. Ongoing data quality checks are compared with laboratory established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

8.1.1 The analyst must make an initial, one-time demonstration of the ability to generate acceptable accuracy and precision with this method (Section 8.2).

8.1.2   In recognition of advances that are occurring in chromatography, the analyst is permitted to improve the separations by changing the GC conditions or column. Each time such a modification is made to the method, the analyst is required to repeat and document the procedure in Section 8.2.

8.1.3   Each day before calibration and after the calibration, the analyst should analyze a reagent blank (instrument blank) to demonstrate that interferences from the analytical system are under control.

8.1.4   With each sample batch, the analyst must analyze a method blank to demonstrate that interferences from sample extraction are under control. Target compounds' concentrations in the blank should be no more than 5x MDL. If blank levels for any component are above 5x MDL and the sample concentrations present in the samples are greater than 10X then the samples may be quantified and qualified. If the blank concentration is greater than 5X MDL and the sample concentrations present in the samples are less than 10 X the blank level, the affected samples should be re-extracted and re-analyzed. If a sample cannot be re-extracted or re-analyzed, the data should be qualified as such. Samples should not be blank corrected.

8.1.5   The laboratory must, on an ongoing basis, demonstrate through the analyses of quality control check standards that the operation of the measurement system is in control. This procedure is described in Section 8.3. The frequency of the check standard analyses is equivalent to 5% of all samples analyzed.

8.1.6   The laboratory must spike all samples with the surrogates to monitor recovery. This procedure is described in Section 8.4.

8.1.7   The laboratory must spike a minimum of five percent or one per batch, which ever is more frequent of all samples in each matrix, with the MSS (Section 6.8.5) to monitor and evaluate laboratory data quality. This procedure is described in Section 8.5.

8.2   To establish the ability to generate acceptable precision and accuracy, the analyst must perform the following operations.

8.2.1   A quality control (QC) check sample concentrate is required containing fuel oil #2 at a concentration of 30 mg/ml in methylene chloride (Section 6.8.4). The QC check sample concentrates must be prepared by the laboratory using stock standards prepared independently from those used for calibration.

8.2.2   Aqueous

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Analyze four 1 L aliquots (TPHC) of the well-mixed reagent water spiked with 0.5 mL QC check sample concentrate and 20 uL of each surrogate according to the method beginning in Section 10.1.

8.2.3 Soil and Sediment

a. Prepare a TPHC QC check sample to contain 200 ug/g of a reference oil (6.8.2) by adding 0.2 mL of QC standard concentrate to 30g of reagent sodium sulfate (6.4). Also add the appropriate surrogates.

b. Analyze four aliquots of silica spiked with QC check standard concentrate according to the method beginning in section 10.3.

8.2.4 For each matrix calculate the average recovery (X) and the standard deviation of the recovery (s) for #2 fuel, using the four results. The average percent recovery should be between 70-120%. samples. The laboratory is to establish the criteria for the standard deviations as described in USEPA Method 8000 A (4).

8.2.5 The FID retention times of the surrogates and internal standards must match the calibration standard as described in 7.2.3.

8.3 The laboratory must analyze a Total Petroleum Hydrocarbon (TPHC) QC check sample with every 5% of the samples. The check sample shall be prepared as directed in Section 8.2.1. The recovery of TPHC shall be in ranges specified in Section 8.2. The FID retention times of the surrogates and internal standards must match the previous calibration as described in 7.2.3.

8.4 As a quality control check, the laboratory must spike all samples with the surrogates chosen in Section 6.8.3 and calculate the percent recovery (P) of the Surrogate based on the FID response.

$$\%P = \frac{A_x}{A_s} \times 100$$

A_x = Area response of SS or IS in check sample

A_s = Average area response of SS or IS in standard

8.4.1 For the surrogate standards, the laboratory must develop separate accuracy statements of laboratory performance for each matrix. An accuracy statement for the method is defined as Percent Recovery ± Standard Deviation (P ± s). The accuracy statement should be developed by the analysis of four aliquots as described in Section 8.2, followed by the calculation of P and s. Alternatively, the

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analyst may use four data points gathered through the requirement for continuing quality control in Section 8.3. The accuracy statements should be updated regularly. The initial recovery may be set 60 to 120 percent.

8.4.2 Calculate upper and lower control limits for %P for the surrogate standard in each matrix.

Upper Control Limit (UCL) = P + 3s
Lower Control Limit (LCL) = P - 3s

The UCL and LCL can be used to construct control charts that are useful in observing trends in performance (14).

8.4.3 The following corrective actions can be taken when the percent recovery of chlorobenzene, androstane and/or tetracosane-d50 are outside of the recovery range:

8.4.3.1 Check calculations to assure there are no errors.

8.4.3.2 Check instrument performance, check the sample preparation procedure for loses due to temperture control and internal standard and surrogate solutions for degradation contamination, etc.

8.4.3.3 Reanalyze the sample or extract if the steps above fail to reveal a problem. If reanalysis yields surrogate recoveries within the stated limites, the reanaysis data should be used.

8.4.3.4 If the surrogate could not be measured because the sample was diluted prior to analysis, qualify the surrogate recovery. If the surrogate co-elutes with a compound (as in coal tar), report only the recovery of the backup surrogate tetracosane-d50. Qualify the out of range surrogate on the data table. No additional corrective action is required.

8.5 Matrix Spike Analysis - The laboratory must, on an ongoing basis, spike (MS) and analyze at least 5% of the samples for each matrix from each sample site being monitored to assess accuracy. The spike should be the matrix spiking standard (MSS) (Section 6.8.5).

8.5.1 Report the recovery as the average of the individual recoveries of the components nC8-nC40, if the hydrocarbon standard is used.

8.5.2 The laboratory should establish there own acceptance criteria for % recovery (R) as in Section 8.2.4. Recoveries of > 70% should be achieved.

8.6 Sample Duplicate - The laboratory must, on an ongoing basis, analyze 5% of the samples for each matrix in duplicate. Both results are to be reported. (No specific criteria concerning the relative precent difference (RPD) exists at this time. However, results should not differ by more than 50%.) The laboratory should establish their own acceptance creteria for RPD based on control charts. A matrix spike duplicate may be used if no postive TPHC samples are in the batch.

8.7 Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

8.8 The laboratory shall determine the method detection limits (MDLs) for the fuels of interest using the methods of 40 CFR 136 Appendix B (7). The MDLs must be confirmed weekly by analyzing a low level standard (2x MDL).

9.0 SAMPLE COLLECTION PRESERVATION

9.1 Aqueous Matrix

9.1.1 Collect a representative water sample in a 1L narrow mouth bottle. A delay between sampling and analysis of greater than four hours requires sample preservation by the addition of 5ml HCl (Section 6.7). Confirmation of a pH < 2 must be obtained in the field.

9.1.2 Sample must be chilled to 4+/-2°C on the day of collection and stored at 4+/-2°C until analyzed.

9.1.3 Samples must be extracted within seven days from the time of collection or five days from verified sample time of receipt (VSTR). Extracts must be analyzed within 40 days of extraction.

9.2 Solid Matrix

9.2.1 Collect a representative soil-sediment sample in a four-ounce, wide-mouth jar with a minimum of air space.

9.2.2 Samples must be chilled at 4+/-2°C on the day of collection and stored at 4+/-2°C until analyzed.

9.2.3 Samples must be extracted within seven days from the time of collection or five days from VSTR. Extracts must be analyzed within 40 days of extraction.

10.0 PROCEDURES

10.1 Dissolved Product

10.1.1 Sealed Extraction (14)

a. Mark the liquid level on the outside of the one liter bottle. Check the sample for floating product. Measure/adjust pH to 2 with 6N HCl if necessary.

b. Add a two inch teflon stirring bar, 30 ul of surrogate standards (Section 6.8.3), and 30 mL of methylene chloride. Seal the sample bottle.

c. Place the bottle on a magnetic stirrer. Adjust the speed so that there is a vortex. Stir for five minutes and then release any pressure. Continue stirring for 15 minutes.

d. Transfer the methylene chloride extract to a serum bottle for storage using a Pasteur pipet. Add 30 mL of methylene chloride to the sample bottle, seal, return to the magnetic stirrer and stir for twenty minutes. Fill the empty sample bottle to the mark with water. Determine the sample volume in a liter graduated cylinder.

e. Combine the methylene chloride extracts, filter and dry the extract through glass wool and sodium sulfate. Adjust the extract volume to 50 mL in a volumetric flask. Store the extract in a 100 mL crimp top serum bottle at 4°C.

f. Emulsions

    1. Emulsions can be broken by centrification

    2. Continuous extraction can be used on samples known to form emulsions, USEPA Method 3520 (4).

g. Screen the extract before concentrating (Section 10.4). Dry and Concentrate the extract as in section 10.1.2.e through 10.1.2i.

10.1.2 Separatory Funnel Extraction (7)

a. Aqueous samples are usually extracted using separatory funnel techniques. If emulsions prevent achieving acceptable solvent recovery

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with separatory funnel extraction, continuous extraction (Section 10.1.2) may be used. The separatory funnel extraction scheme described below assumes a sample volume of 1 L. When a sample volume of 2 L is to be extracted, use 250, 100 and 100-mL volumes of methylene chloride for the serial extraction.

b. Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour the entire sample into a 2 L separatory funnel. Measure/adjust pH to 2 with 6N HCL. Pipet 30 uL of the surrogate standard spiking solution into the separatory funnel and mix well (Section 6.8.3).

c. Add 60 mL of methylene chloride to the sample bottle, seal and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min.

If the analyst must employ mechanical techniques to the complete phase separation, the optimum technique depends upon the sample. The techniques may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250 mL Erlenmeyer flask with a glass stopper.

If the emulsion cannot be broken (recovery of less than 80% of the methylene chloride, corrected for the water solubility of methylene chloride), transfer the extract to the chamber of a continuous extractor and proceed as described in Section 10.2.3.

d. Add a second 60 mL volume of methylene chloride to the sample bottle and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner. Label the combined extract. Screen the extract (Section 10.4) before concentrating.

e. Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D concentrator if the requirements of Section 8.2 are met.

f. Pour the combined extract through a solvent rinsed drying column (Section 5.3.10) containing about 10 cm of anhydrous sodium sulfate, and

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collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

g.   Add one or two clean boiling chips and attach a three-ball Snyder column to the evaporative flask for each fraction. Prewet each Snyder column by adding about 1 mL of methylene chloride to the top. Position the K-D apparatus in a hot water bath (60°C to 65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of the distillation the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with one to two mL of methylene chloride. A five mL syringe is recommended for this operation.

h.   Add another one or two clean boiling chips to the concentrator tube of each fraction and attach a two ball micro Snyder column. Prewet the Snyder column by adding about 0.5 mL of methylene chloride to the top. Place the KD apparatus on a hot water bath and allow it to drain and cool for at least 10 min. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with approximately 0.2 mL of methylene chloride. Adjust the final volume to 1.0 mL with the solvent. Transfer to a 1 ml GC autosampler vial and add 20 uL of the GC internal standard (5-androstane). If the internal standard method is used.

i.   Determine the original sample volume by refilling the sample bottle to the mark with water and transferring the liquid to a 1000 mL graduated cylinder. Record sample volume to the nearest five mL.

j.   Other extract concentration methods can be used if the recoveies of the surrogates and the QC check samples meet the requirements of the method.

10.2.3 Continuous Extraction (4)

a.   Mark the water meniscus on the side of the sample bottle for later determination of sample volume. Transfer the sample to the continuous

extractor. Measure/adjust pH to 2 with 6N HCL. Using a pipet, add 30uL of surrogate standard spiking solution and mix well. Add 60 mL of methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor.

b. Repeat the sample bottle rinse with an additional 50 to 100 mL portion of methylene chloride and add the rinse to the extractor.

c. Add 200 to 500 mL of methylene chloride to the distilling flask, and sufficient reagent water to ensure proper operation, and extract for 24 hours. Allow to cool, then detach the distilling flask. Screen the extract (Section 10.4) before concentrating. Dry and concentrate the extract as in section 10.1.2.e through 10.1.2.i.

10.3 Sample preparation, soils and sediments (1,12)

10.3.1 Homogenize the soil sample with a solvent-rinsed stainless steel spatula. Weigh about five grams of the sample to +.01g into a tared aluminum pan. Dry at 105 degrees Celsius for 12 hours and calculate the percent solids content (Section 11.3.4).

10.3.2 Soxhlet Extraction - If the samples contain residual oil and tar, the EPA soxhlet extraction method 3540 should be used (2). Method 3540 may be used for all sample types.

a. Quickly blend 10-30g of the solid sample with 10-30g of anhydrous sodium sulfate and place in an extraction thimble. The extraction thimble must drain freely for the duration of the extraction period. A glass wool plug above and below the sample in the Soxhlet extractor is an acceptable alternative for the thimble. Add 30uL of the surrogate standard spiking solution onto the sample. The blending of the soil with the anhydrous sodium sulfate can lead to the loss of volitile components (C8-C12). If the sample is expected of containing a large volitle component such as Jet fuel, this drying process may be omitted.

b. Place 300 mL of the extraction solvent into a 500-mL round-botton flask containing one or two clean boiling chips. Attach the flask to the extractor and extract sample for 16-24 hours at 4-6 cycles/hr.

c. Allow the extract to cool after the extraction is complete. Screen the extract before continuing (Section 10.4). Dry and concentrate the extract as in Section 10.1.2e through 10.12h.

10.3.3 Gyrotory Shaker Extraction

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a.	Add 30g (+/- .1 g) (wet weight) of the sample with a stainless steel spatula to a 250 mL acid-cleaned, solvent-rinsed, capped Erlenmeyer flask. Mix in 30 g of sodium sulfate. If the sample has excessive moisture, add additional amounts of sodium sulfate. This procedure must be done quickly to reduce evaporation losses.

b.	Add 50 mL of methylene chloride, 30 uL of surrogate standard spiking solution, screw on the top, and shake the mixture vigorously for 1 minute, vent the flask (Section 6.8.3).

c.	Place the 250 mL flask on a rotary shaker unit, positioned behind a safety shield, in a fume hood. Adjust the agitation rate of the shaker device to 400 RPM and extract the samples under these conditions for exactly 30 minutes.

d.	After 30 minutes, the rotary shaker should be turned off and Erlenmeyer flasks removed to a stationary location. The analyst should permit suspended solids and particulate matter in the flasks to settle for approximately 30 minutes.

e.	Using a pasteur pipet, carefully transfer the supernatant extract to a 100 mL crimp top serum bottle for storage. Do not agitate the sediment layer.

f.	Extract the sample with two additional 30mL volumes of methylene chloride. The sample should be sonicated for 0.5 minutes before the last extraction. This will insure the complete dispersion of the soil. Combine all of the extracts, in the serum bottle for storage. Screen the extract before continuing (Section 10.4). Dry and concentrate the extract as in section 10.1.2e through 10.1.2.h.

10.3.5 Other Extraction Methods

a.	Extraction methods listed in SW846 may be used such as 3545 Pressurized Fluid Extraction, 3541 Automated Soxhlet Extraction and 3550 Sonication.

b.	The laboratory must conduct a one time demonstration of the ability to

generate acceptable accuracy and precision (Sectin 8.2). The demonstration must include comparison results with real samples that cover the C8-C40 carbon range. The laboratory must meet the sensitivity

requirements of Section 2.3.3, the dynamic range of section 2.3.4, and the surrogate recovers of section 8.4.1.

c.   Routine analysis using alternate extraction methods must meet the surrogate reqiurements of section 8.4.1.

10.4 Preliminary Analysis of Extracts (Screening)

10.4.1 Adjust the chromatograph for maximum sensitivity.

10.4.2 Inject 1 uL of the sample extract using an auto sampler.

10.4.3 A complete profile of the extract should be obtained without saturating the detectors. The largest peak should be a minimum of 50% and a maximum of 90% full span. If the response is too high, the extract should be diluted. if the response is too low, concentrate the extract. If the response meets the criteria, determine the extract volume and go to section 10.5 or 10.6.

10.5 Cleanup for Quantitation (4)

10.5.1 Should the sample require additional cleanup due to interfering compounds, polar compounds or a large unresolved hump without destinct peaks, in the chromatogram, use EPA Method 3630 - silica gel cleanup. Combine fraction 1 (pentane; aliphatics) and fraction 2 (methylene chloride/pentane [2: 3 v/v] aromatics) for total petroleum hydrocarbons (TPHC) analysis.

10.6 Chromatographic Analysis

10.6.1 One milliliter of extract ready for analysis should be transferred to a one mL GC auto sampler vial.

10.6.2 All extracts, standards and blanks, should contain the GC internal standard (30 ug/L) when applicable.

10.6.3 Inject one to two uL of extract using an autosampler device or the solvent plug method.

10.7 Recommended Chromatographic Conditions (21)

10.7.1   Temperature Program for RTX-1 Column:

Initial Value   40°C
Initial Time   2.00 min

Program Rate 12.00°C/min
Final Value   320°C
Final Time   10 min
Total Run Time   35 min
Carrier Gas   He

10.7.2 Injection Port Temperature   330°C

10.7.3 Detector Temperature   330°C

10.7.4 Instrument Performance

a. All of the peaks contained in the standard chromatograms must be
    sharp and symmetrical. Peak tailing must be corrected. If only the
    compounds eluting before ethylbenzene give random response, have
    unusually wide peak width, are poorly resolved, or are missing, the
    problem is usually traceable to the injection port temperature.

b. Check the precision between consecutive QC check samples. A properly
    operating system should perform with an average relative standard
    deviation of less than 10%. Poor precision is generally traceable to
    pneumatic leaks.

c. Monitor the retention time for each analyte using data generated from
    calibration standards. If individual retention times vary by more than ±3
    standard deviations (7.1.1) over a twelve hour period, the source of
    retention data variance must be corrected before acceptable data can be
    generated.

d. The instrument sensitivity must be maximized. Injection of 2ul of a
    1ng/ul hydrocarbon standard should yield a detector signal-to-noise ratio
    of between 5:1 and 15:1 for the individual alkanes.

10.8   Analysis Sequence

10.8.1 This method uses a 12hr clock. The time sequence begins with the analysis of
       the first initial calibration standard. Continuing calibrations must be verified
       every 12hrs.

10.8.2 Sequence

1. Instrument Blank
2. Initial Calibration

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3. Samples (including Method Blanks, and QC samples)
4. Continuing Calibration (every 12hrs.)

11.0 CALCULATIONS

11.1 Concentration of Petroleum Hydrocarbons

11.1.1 To calculate the concentration of total petroleum hydrocarbons in the sample, the area response attributed to the petroleum must first be determined. This area includes all of the resolved peaks and the unresolved "envelope". This total area must be adjusted to remove area response of the internal standards, solvent, surrogates and the GC column bleed.

11.1.2 Establishing the baseline

Baseline response within ± 20%

a. Column bleed is defined as the reproducible baseline shift that occurs during temperature programming of the GC column oven. To determine this area, a methylene chloride blank injection should be analyzed at the beginning of the day and after every 12 hours to determine the baseline response. The baseline is then set at a stable reproducible point just before the solvent peak. This baseline should be extended horizontally to the end of the run. The area for the blank run that must be subtracted from the actual sample run, includes all of the area between C_8 and C_{40}.

b. The baseline for the sample should be set in the same manner. The area in the sample will contain the area attributed to petroleum and that attributable to the baseline. The petroleum area must be calculated by subtracting the baseline area and area for the *internal* standards from the total area. The TPHC is then calculated according to the equation in Section 11.1.4.

c. As the concentration of TPHC in the sample approaches the detection limit, the baseline correction becomes more critical.

11.1.3. Mass discrimination must be kept to a minimum by placing a small plug of silanized glass wool one cm from the base of the glass injection liner. The capillary column should be placed just below the glass wool. A full range alkane standard should be run to test the degree a mass discrimination before performing any actual sample analyses. The reponse factor ratio of C_{32}/C_{20} should be greater than 0.8. If less than 0.8, reposition the column in the glass liner until the mass discrimination is minimized.

11.1.4 Concentration based on Internal Standard

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a.   From sample analysis, determine the total area (A) of the unknown and calculate the concentration. The analyst must take care when calculating total product areas that the appropriate baseline is used.

(1)   Aqueous Matrix

$$C = \frac{(A)\ (C_{is})\ (D)\ (Ve)}{(RRF)\ (A_{is})\ (V_o)\ (Vi)}$$

Where:

C   =   Concentration of Analyte or concentration of Total Petroleum Products, ug/L

A   =   Area response of compound or TPH to be measured.

D   =   Dilution Factor

C_{is} =   Concentration of internal standard added to extract

A_{is} =   Area response of internal standard

RRF   =   Relative response factor of analyte (section 11. 2.2). For TPHC RRF is the average of all the nC8-nC40 RRFs.

V_e = Final volume of extract, uL

V_1 = Volume of extract injected, uL

V_o = Volume of sample, L

(2) Soil and Sediment

$$C = \frac{(A)\ (C_{is})\ (D)\ \ Ve}{(RRF)\ (S)\ (A_{is})\ \ Vi}$$

C =   Concentration of compound to be measured, or Concentration of TPHC, ug/g

S =   Dry sample weight, grams

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11.2   The FID Relative Response Factor (RRF) calculation for a specific compound or TPHC.

$$RRF = \frac{C_{is} \times A_{cs}}{A_{is} \times C_{cs}}$$

Where: C_{cs} =   Concentration of calibration compound or TPHC standard, ug/ml

C_{is} =   Concentration of internal standard, 5-androstane, ug/ml

A_{is} =   Area Response of internal standard

C_{cs} =   Area of calibration compound or TPHC standard

11.3   External standard calibration - The concentration of each analyte in the sample may be determined by calculating the amount of analyte injected, from the peak response, using the calibration curve or the calibration factor determined in Step 7.1.3. The concentration of a specific analyte is calculated as follows:

(1)   Aqueous samples

$$Concentration\ (ug/L) = \frac{(A)\ (D)\ (Vc)}{RF\ (V_o)\ (Vi)}$$

RF = Response factor of analyte (Section 7.1.2) or TPHC average response of all th nC8 - nC40 RFs.

(2) Nonaqueous

$$Concentration\ (ug/g) = \frac{(A)\ (D)\ (Vc)}{RF\ (s)\ (Vi)}$$

11.4   Matching Chromatographic Patterns - The following provides the basis for identification of the type of petroleum product. Method OQA-QAM-018 should be used to make more definative identifications.

11.4.1 Interpretation (from ASTM D 3328, (1))

a.   Basis of Matching - The source of a spilled petroleum oil can be identified by comparison of the chromatogram to that of a suspected source oil or

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that of a reference oil. Identical petroleum products give identical chromatographic peak patterns.

b. Chromatogram Features - The major features of the chromatogram that are used for comparison are listed as follows:

A FID chromatogram shows the features of a homologous series of normal paraffins, the isoprenoid hydrocarbons pristine and phytane, the other resolved peaks and the unresolved envelope. All of these features are used to characterize petroleum oil.

c. Weathering effects: - When petroleum is spilled on open water or spilled on open ground, weathering will progress rapidly. A thin slick on open water may lose significant amounts of its components, up to nC15, 271°C, atmospheric boiling point, within 48 hours of being spilled. Soil samples will lose the soluble fraction through leaching. Biological degradation of petroleum begins within seven days. It is important to be aware of the effects of weathering when matching chromatograms of spill samples more than a few hours old. It is advisable to compare only those portions of chromatograms boiling above pentadecane in order to minimize the difference resulting from weathering. Reference oils can be weathered in the laboratory using the method of Reference 10.

Light distillate fuels cannot survive heavy weathering and have few hydrocarbons above C15. Comparison of the residues of these oils can only be done qualitatively - from about C8-C15.

d. A direct comparison of chromatograms will establish identity or nonidentity between samples. The comparison involves a peak-for- peak matching, noting differences or similarities in relative peak height. If the chromatograms are the same on the basis of the peak-for-peak matching, there is a high probability that the samples are from the same source. A mismatch occurs when the chromatograms are different. The differences may be due to the presence of one or more components or petroleum products in one sample relative to another. Spill samples may contain components such as cleaning detergents, plasticizer, paint vehicles, etc. The presence of one or two components in a spill sample which are absent in a suspect petroleum oil is not absolutely indicative of non-identity.

e. If the ratio of pristine/phytane in the unknown and reference petroleum oil match with ± 15%, the fingerprint match is confirmed.

11.5 Percent Recovery of Surrogate Standard (5)

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Percent recovery is calculated using the 5-androstane GC internal standard, (C_{is}).

$$\% \text{ SS recovery} = \frac{(A_{ot})(C_{is}) \quad \times 100}{(C_{ot})(A_{is})}$$

Where: C_{ot} = Concentration of surrogate

A_{ot} = Area of surrogate

SS = Surrogate

Percent recovery based on External Calibration

$$\% \text{ SS recovery} = \frac{C_{of}}{C_{ot}} \times 100$$

Where: C_{of} = Concentration of surrogate found

11.6   Percent Solids (P)

$$P = \frac{D_s}{T_s} \times 100$$

D_s = Weight dry Sample, g

T_s = Weight wet Sample, g

11.7   Dry Weight (S)

$$S = \frac{\text{Wet Weight} \times P}{100}$$

12.0   REPORTING REQUIREMENTS AND DELIVERABLES

The following minimal information must be provided to the Department on request. The Laboratory must keep this information on file and available for inspection by the Department as per N.J.A.C. 7:18 (16).

12.1 Chain of custody documents. For every sample submitted to the laboratory, both field and laboratory chain of custody documents MUST be provided at the end of the final data report. The chain of custody must show the signatures of the sample custodian, extraction supervisors and any other personnel who handled the sample. It must clearly track the movement of the sample through the laboratory by showing the relinquishing and acceptance of the sample by each person.

12.2 Methodology Review

The laboratory shall provide a brief narrative outlining the essential points of each method actually employed in the analysis of the samples submitted to the laboratory.

12.3 Non-Conformance Summary Report

The laboratory shall describe in narrative and/or tabular from any item which does not conform to the requirements of this method. This shall include but is not limited to a discussion of missed holding times, of failed Quality Assurance/Quality Control criteria, sample matrix effects on the analysis, sample dilutions, re-analyses, corrective actions taken and deviations from the analytical method specified on the analytical request form or the preparative methods permitted.

12.4 Sample Data Package - must contain the following information in sequence:

12.4.1 Quantitative Sample Results Summary (uncorrected for blank), Blank Results and Method Detection Limits.

12.4.2 Qualative Sample Result Summary (For fingerprint work)

12.4.3 Quantitation Reports

12.4.4 Sample Chromatograms

The chromatograms must be clearly labeled with the following information:

a. Sample identification number.
b. Volume injected.
c. Date and time of injection.
d. GC Column identification.
e. GC instrument identification - exact instrument employed.
f. Positively identified compounds, either directly above the peak or on a printout of retention times, if the retention times are printed on chromatograms.
g. Internal Standards labeled.

h.   Surrogate labeled.

i.   Analyst signature.

12.5   Quality Control Summary - must contain the following items:

a.   Surrogate Recovery Summary

b.   QC Check Sample Recovery

c.   Method Blank Summary

d.   Matrix Spike Summary

e.   Duplicate Summary

12.6   Standard Data Packages - must contain the following items:

a.   Initial Calibration Data Summary

b.   Continuing Calibration Data Summary

c.   Chromatograms of Standards and Quantitation Reports

d.   Chromatograms of Reference Standards where applicable

12.7   Raw QC Data Package - additionally must contain the following items:

a.   Blank Chromatograms

b.   QC Check Sample Chromatograms

c.   Blank spike Chromatograms.

12.8   Qualitative Sample Results Summary - List Sample Fingerprint matches (ASTM D3328(I)).

a.   Based upon the visual comparison of source chromatograms, and after considering weathering, report the sample of unknown origin as belonging to one of the categories below:

1.   Match - The chromatogram is identical to one, or more, of the samples submitted for comparison.

2.   Probable Match - The chromatogram is similar to one, or more, of the samples submitted for comparison, except: (a) for changes which can be attributed to weathering, or (b) differences attributable to specific contamination.

3.   Indeterminate - The chromatogram is similar to one, or more, of the samples submitted for comparison, except for certain differences as in 2, of such magnitude that it is impossible to determine whether the

unknown is the same petroleum oil heavily weathered, or a totally different oil.

    4.   Mismatch - Unlike the samples submitted for comparison.

  b.   Compare unknowns to a library of the products listed in Section 1.1.

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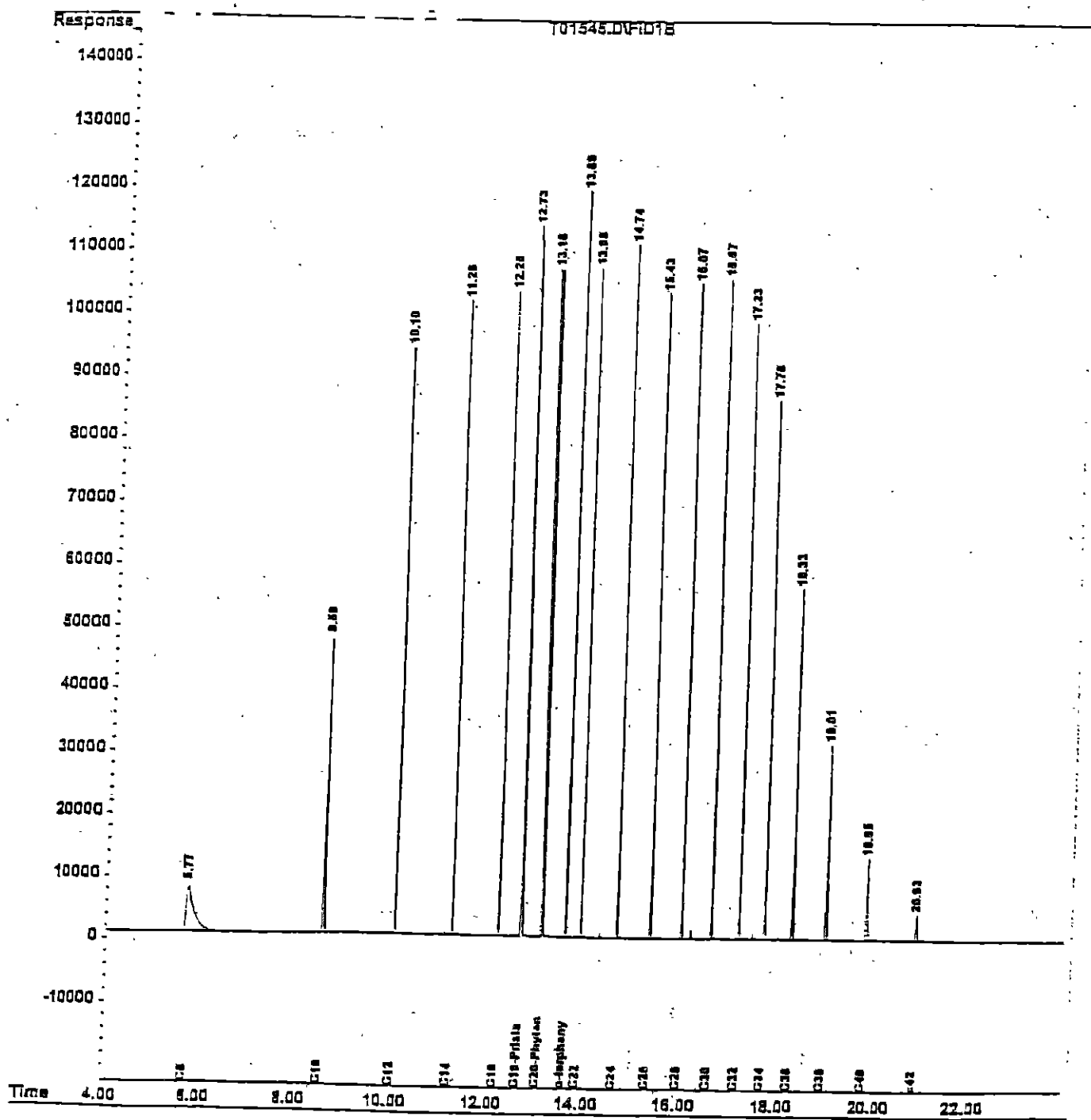# Figure 1 - Calibration Standard 50 ug/Kg (C8-C42)
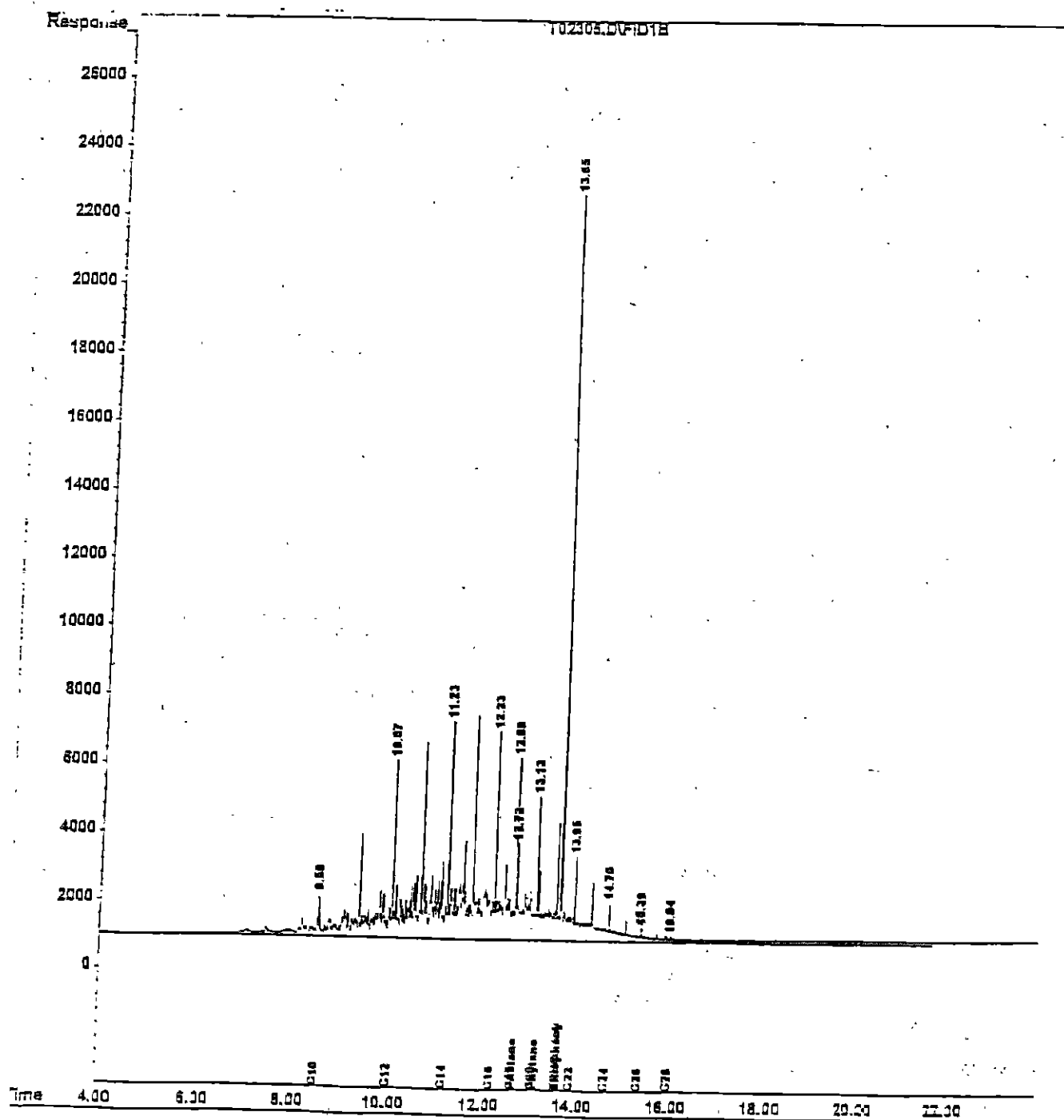
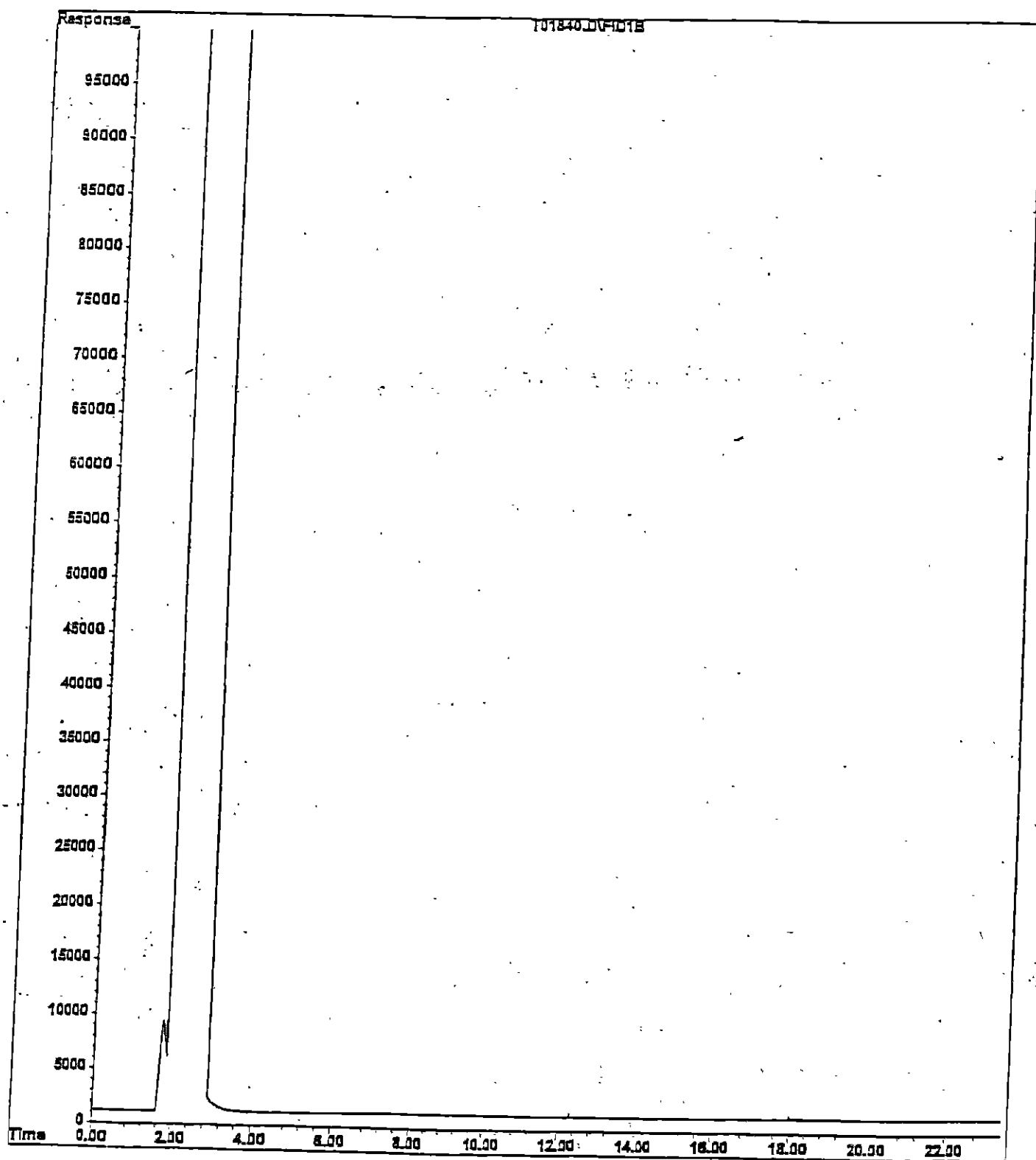Figure 2 - MDL Study 250 ug/Kg in Soil

Figure 3 - Methylene Chloride Blank

Figure 4 - Diesel Fuel #2 / Methylene Chloride Soxhlet Extraction